

ADHESION TENSION. A RECEDING
CONTACT ANGLE, PRESSURE OF
DISPLACEMENT METHOD

A DISSERTATION

Submitted in partial fulfillment of the requirements
for the DEGREE OF DOCTOR OF PHILOSOPHY in the
University of Michigan

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CHARLES E. WHITNEY

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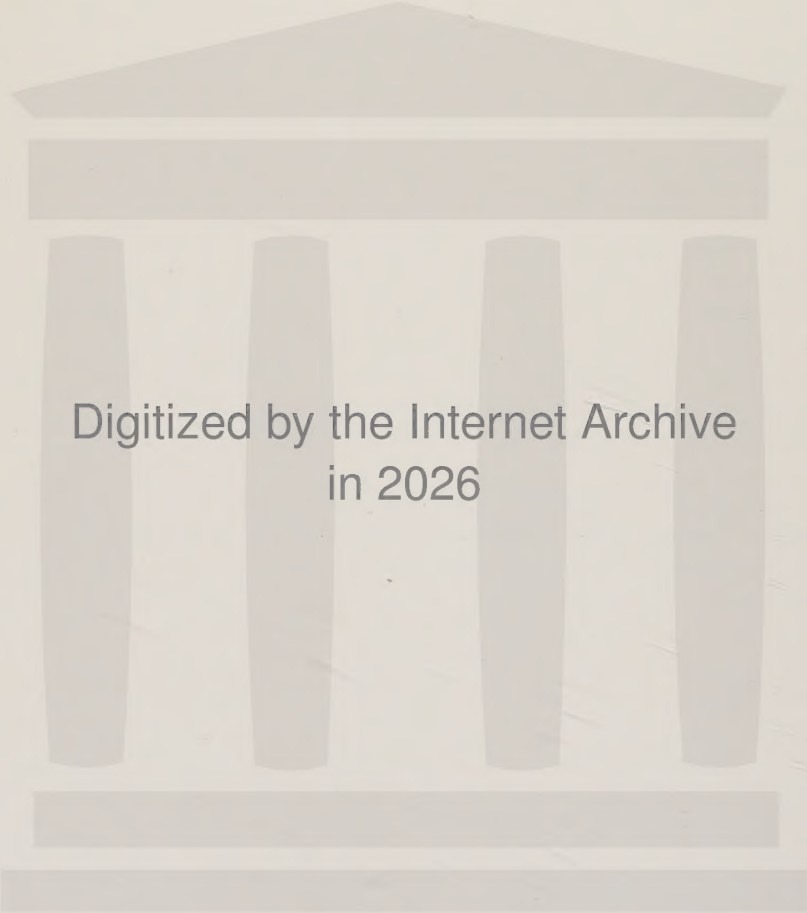
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ADHESION TENSION

A Receding Contact Angle, Pressure of Displacement Method

During the past five years a number of investigations have been reported in which adhesion tension values of certain solid-liquid systems have been obtained. In nearly all of these investigations the original pressure of displacement method of Bartell and Osterhof¹ was used. With this method finely divided solid material is compressed into a membrane. Liquid is brought into contact with this membrane and the pressure is measured which is just sufficient to prevent movement of liquid through its pores. At the very beginning of the experiment liquid is allowed to advance, but very shortly thereafter further advance is prevented by gradually building up an opposing pressure. Advance of liquid is detected by noting movement of liquid in the indicator tube attached to the low pressure side of the system.

At the time of the original pressure of displacement work it was assumed that one and only one definite equilibrium contact angle was possible for any given solid-liquid-air (or solid-liquid-liquid) system. The existence of advancing and of receding angles was well known, but it was assumed, at least by us, that either an advancing or a receding angle would, within a short time, so adjust itself as to give finally a definite equilibrium angle which would be the same whether approached from the advancing or the receding angle. We have since obtained good evidence that advancing angles and receding angles may each exist as definite, but different, equilibrium angles. A careful consideration of the precise method used in the earlier work led us to believe that the periodic increases in pressure imposed upon the system gave a final pressure which in nearly every case was ascribable to the effect of the receding equilibrium angle; we could not be absolutely certain, however, that this was actually the case.

Somewhat over two years ago an attempt was made in our laboratory to construct an apparatus with which a liquid system advancing by capillarity within the pores of the membrane would automatically build up a pressure which would reach a maximum value and would then serve as a measure of the balancing or equilibrium pressure. Throughout the operation of this method the contact angle would at all times be of the advancing type. At present we need state only that much difficulty was encountered in our attempts to obtain reproducible values. The details of this work will be presented in another paper. A still later investigation on contact angles, in our laboratory (unpublished), has shown that receding angles are more easily reproducible than are advancing angles. In view of the above findings it was decided to carry

¹ Bartell and Osterhof: Colloid Symposium Monograph, 5, 113 (1927); Ind. Eng. Chem., 19, 1277 (1927); Z. physik. Chem., 130, 715 (1927); J. Phys. Chem., 34, 1399 (1930).

out an investigation in which the displacement pressure apparatus would be so operated that receding contact angle measurements would of certainty be obtained. In carrying out this plan the membrane pores were first completely filled with liquid and then the minimum pressure required to force back the liquid column was determined.

Experimental

Apparatus.

Displacement Cell. An assembled cell and its parts are shown diagrammatically in Fig. 1. The cells were similar in construction to those used by

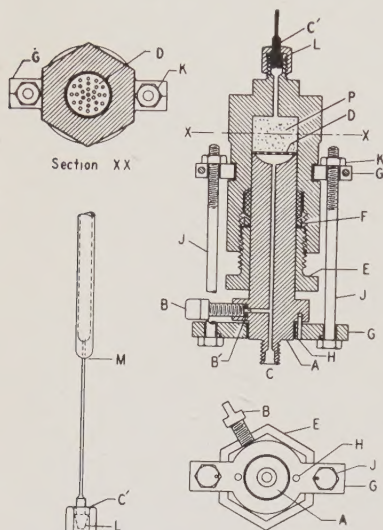


FIG. 1

Assembly and Details of Cell

Bartell and Osterhof.¹ They were shorter, the chamber being about 23 mm in length; one end was solid except for a small outlet to which a connection was made with a manometer. A glass capillary indicator tube was attached to the other end of the cell.

Manometer. The manometer was of the simple U-tube type with an auxiliary or third arm. One arm of the manometer was of 7 mm glass tubing. This was sealed to a ground-glass joint by means of which the connection was made with the cell. The second arm was a capillary tube in which the mercury level was regulated and observed. The third or auxiliary arm was joined to the bottom of the U-tube next to the capillary arm. It was provided with a stopcock with which it could be shut off from the rest of the manometer.

The main purpose of this third arm was to serve as a reservoir making possible a gradual lowering of the mercury in the capillary tube. At the lowest part of the manometer was a capillary outlet consisting of a stopcock and a drawn-out tip. This outlet was for the purpose of removing mercury slowly in order to bring about a gradual decrease of pressure within the manometer system. The connection from the manometer to the cell consisted of a ground glass joint above which was a 3-way stopcock. Above the stopcock was a small bulb and beyond this was a copper tube attached to a small union C, C', L (Fig. 1) with which final connection was made.

Packing Apparatus. A method was developed for packing a powder into the form of a membrane so that a given amount of either wet or dry powder might be used and give essentially the same volumes.² The packing or tamping machine used for packing the powder in the the cell was developed by Bartell and Jennings.² Briefly, it consisted of a packing plunger 2.5 kilograms in weight which was raised by turning a crank and caused to fall on

² Bartell and Jennings: unpublished.

the powder in the cell. A suitable device held the cell in position and kept the plunger in alignment during its fall. The apparatus was adjusted so as to allow the plunger to fall a distance of 85 mm.

Thermostat. The experimental determinations in this work were all carried out in an air thermostat at 25°C. The temperature was controlled to within 0.1°C.

Materials.

Silica. The only solid used in this work was silica, a ground Ottawa sand of fairly high purity. It was twice treated with boiling 1:1 HCl, then with hot water and filtered. The silica was then washed with boiling water about twenty times. It was dried in an oven at 100°C and muffled at red heat for about 2 hours. It was graded by sieving, about three-fourths of it passed thru at 350 mesh, the remainder was discarded. This screened powder contained not only particles which would just pass thru the sieve but also much very fine powder which if shaken up with water would not settle out for several days. Such variation of particle size was not desirable as the pore size of the compressed membranes formed with it would not be uniform. In order to obtain a smaller range of particle size, the silica which had passed thru the 350 mesh sieve was stirred up in a large crock of distilled water and was allowed to settle for 30 minutes. The suspension which had not settled out was siphoned off and the settled powder was carried thru this sedimentation process again. The settled powder was then dried and again muffled at red heat for 2 hours.

A test was made to determine whether the surface tension of liquids would be altered by standing in contact with this silica. Some of it was shaken with pure water. After removal of the silica by centrifuging, there was no change in the surface tension of the water. This indicated absence of water soluble impurities in the silica.

Liquids. All of the liquids used in this work were of good grade, though not of "highest purity." Determinations of the surface tensions of the liquids gave values which were in good agreement with accepted values.

Experimental Procedure.

Packing. The cell was placed in the packing apparatus. A small circular piece of linen cloth was placed in the bottom of the cell. This was to prevent silica being forced or blown out of the cell by the fall of the packing plunger upon the silica. Approximately 1 gram of silica was placed in the cell and a piece of cloth inserted on top of it. The silica was then subjected to 50 impacts of the plunger. About 6 one-gram increments of silica were used for the preparation of the membrane. The top cloth was removed before each addition of silica and then replaced for each packing operation.

Measurement of Pressure and Determination of Pore Size. After a cell had been packed it was assembled as shown in the diagram in Fig. 2. The liquid (a liquid which forms zero contact angle with the solid) was then drawn into the cell so as to wet the membrane completely. The tube connecting to the

manometer was filled with liquid as far as the stopcock. It was then joined to the cell by means of the union. The cell was set up as shown in Fig. 1, and the connection to the manometer made by means of the ground-glass joint. The mercury level in the manometer was raised until mercury filled the 3-way stopcock. This stopcock was turned so as to make direct connection between the mercury and the liquid which extended into the cell. The mercury and liquid interface was then raised by loosening the valve, (*B* of Fig. 2), and raising the mercury level in the manometer. In this way the level of this interface was raised into the small bulb. Correction was made for the capillary depression of mercury in the capillary as well as for the liquid column which extended from the mercury level in the bulb to the cell. Since the final "negative" pressure was measured by the difference in the levels of the mercury in the bulb and in the capillary these corrections could be made simultaneously by noting the difference in levels of the two mercury menisci when the valve, *B*, was open, or in other words when both columns were open to the air. After making this reading the valve was tightly closed. The indicator tube was then connected to the other end of the cell. A column of colored liquid was placed in this indicator tube to show when movement of the liquid in the cell occurred. The cell and manometer thus assembled were ready for the determination of the displacement pressure.

With the auxiliary arm of the manometer in direct connection, the outlet tube at the bottom of the manometer was partially opened. This was adjusted so as to give a very gradual lowering of the mercury in the capillary and auxiliary tubes. The pressure differential was thus increased slowly until the liquid in the indicator tube began to move. The pressure was then allowed to remain constant for a few minutes until the indicator liquid again became stationary. This procedure was repeated until the liquid showed a continuous movement in the cell towards the manometer. The success of the measurement is dependent upon a sufficiently slow and careful increase in the pressure differential. The pressure differential (*i.e.*, "negative pressure") which caused the continuous movement of the liquid was regarded as the equilibrium displacement pressure corresponding to the receding contact angle. Strictly speaking, this pressure was that required to draw air into the liquid-filled pores rather than the pressure required to prevent the displacement of air from the pores by the liquid. The small movements of the liquid which occurred before the maximum or equilibrium pressure was reached were attributed to displacement of the liquid from the linen disc at the end of the membrane and also to variations in the pore radii of the membrane. A pressure less than the equilibrium pressure was sufficient to initiate movement in a few large pores and this movement continued until smaller pores were reached. The movement of the liquid became continuous when the maximum pressure for the effective pore radii was reached, for at this pressure the liquid was probably moving in practically all of the larger pores.

A similar method was tried out in which the pressure was positive, *i.e.*, pressure was built up by increasing the mercury head on the high pressure side of the system. The pressure was measured which was just sufficient to drive

liquid through the membrane. The results thus obtained give good agreement with those reported herein. The "pull method" is limited in use to systems in which the displacing pressure is not greater than atmospheric pressure.

From the maximum (equilibrium) pressure values obtained the pore size was calculated by the equation,

$$r = \frac{2S}{hdg} = \frac{2S}{Pg}^*$$

Data obtained in measurement of pore size of the silica membranes used are given in Table I.

TABLE I

Determination of Pore Size of Compressed Silica Powder Membranes

System	P grams/cm ²	S dynes/cm	r $\times 10^{-4}$ cm
Water—Air—Silica	469	72.08*	3.13
Water—Benzene—Silica	229	34.76**	3.10
Water—Nitrobenzene—Silica	166	25.32**	3.10
Average			3.11

* Surface Tension

** Interfacial Tension

It might be mentioned that Bechhold,³ and Bigelow and Bartell,⁴ as well as others have measured pore radii of porous membranes by determining the pressure required to force liquid out of the pores. In principle that method and this one are essentially the same.

We found it possible to measure pore size by means of liquid-liquid as well as liquid-air systems. Bartell and Greager⁵ measured interfacial tensions by a displacement pressure method in a porous membrane of calcium fluoride. Bechhold and Schnurmann⁶ have also used liquid-liquid systems to measure pore size of porous membranes and found that the values agree closely with those obtained with liquid-air systems. In carrying out similar measurements in this work the compressed membrane was first wetted completely with water and the water-organic liquid interface was then drawn into the pores. The pressure required to prevent displacement of the organic liquid by the water was then measured.

Determination of Adhesion Tension of Contact Angle Forming Liquids. The determination of the adhesion tension of liquids, which in contact with air

* The symbols used in this paper are the same as those used in recent publications from this laboratory, namely: S_1 = Surface tension or free surface energy of solid phase; S_2 = Surface tension or free surface energy of liquid phase; S_3 = Surface tension or free surface energy of water.

A combination of subscripts refers to interfacial tension values as S_{23} = interfacial tension of organic liquid against water, S_{12} = interfacial tension of organic liquid against solid, etc. θ represents the angle of contact, P represents the displacement pressure, and g represents the gravitational constant.

³ Z. physik. Chem., **64**, 328 (1908).

⁴ J. Am. Chem. Soc., **31**, 1194 (1909).

⁵ Unpublished work completed in May, 1929.

⁶ Z. physik. Chem., **142**, 1-24 (1929).

form contact angles with silica, was readily carried out by measuring the contact angle formed in each case. The membrane was completely wetted with the contact angle forming liquid, the cell and manometer set up, and the pressure differential increased until the liquid started to be pulled back through the cell. (The pressure at which this occurred was lower than that corresponding to the force of surface tension of the liquid and the extent of this lowering is directly related to the magnitude of the receding contact angle.) The auxiliary arm of the manometer was then shut off from the capillary by means of the topcock provided for that purpose, the mercury in the capillary began to rise as the liquid within the membrane receded. After a period of time this movement ceased and the liquid became stationary as did the mercury column in the manometer. The pressure remained constant at that point for several hours. This pressure value was quite reproducible and was considered to be representative of the receding equilibrium contact angle. The contact angle was calculated by use of the equation,

$$\cos \theta = rPg/2S. \quad (2)$$

The adhesion tension, A_{12} , of the contact angle forming liquid was calculated by use of the equation,

$$A_{12} = S_2 \cos \theta, \quad (3)$$

or from the more general equation,

$$A_{12} = S_2 K,$$

in which K may be considered as the adhesion constant which may have a value greater than unity. Adhesion tension values were determined for five liquids which form contact angles against silica and are to be found in Table II.

TABLE II
Adhesion Tension Determinations of Contact Angle-Liquids
Organic Liquid—Air-Silica

	$r = 3.11 \times 10^{-4} \text{cm}$				
	P grams/cm ²	θ	$\cos \theta$	S_2 dynes/cm	A_{12} dynes/cm
Acetylene tetrabromide	281	29°25'	0.874	49.07	42.8
Alpha Brom-naphthalene	260	25°43'	0.901	44.00	39.6
Alpha Chlor-naphthalene	256	18°44'	0.947	41.20	39.0
Bromoform	245	23°56'	0.914	40.93	37.4
Iodobenzene	243	18°00'	0.951	39.10	37.2

Determination of the Adhesion Tension of Water. The adhesion tension of water against silica was determined by the measurement of the contact angles formed by liquid-liquid-solid systems. The organic liquid used was one which forms a contact angle with silica and whose adhesion tension against silica had been measured as previously described. The determination of the interfacial contact angle formed by the water-organic liquid interface against silica required a slightly different procedure from that used for the determination of

the solid-liquid-air angles previously described. The compressed powder membrane was wetted completely with the contact angle forming liquid and then a small increment of silica wetted with water was packed on top of the silica wetted with the organic liquid. The cell was then assembled and set up as in previous measurements. The pressure differential was increased slowly within the system until movement of the liquids in the cell ceased. When this occurred the auxiliary arm of the manometer was shut off as in the previous determination and the system allowed to attain equilibrium. This was assumed to have been reached when the pressure differential was so great that there was no more displacement of the organic liquid by the water. The interfacial contact angle was then calculated by means of the equation,

$$\cos \theta_{23} = rPg/2S_{23}. \quad (4)$$

Since the adhesion tension, A_{12} , of the contact angle forming liquid was known and the value of the contact angle of the interface likewise known, the adhesion tension, A_{13} , of water against silica was calculated by means of the equation,

$$A_{13} = A_{12} + S_{23} \cos \theta_{23}. \quad (5)$$

Five separate determinations of the adhesion tension of water against silica were carried out using water with each of the five contact angle forming liquids previously mentioned. These results are to be found in Table III.

Determination of the Adhesion Tension of Zero Contact Angle Liquids. The determination of the adhesion tension of organic liquids which form a zero contact angle with silica was carried out by the measurement of interfacial contact angles. In this case, however, the adhesion tension of water was known and the adhesion tension, A_{12} , of these organic liquids was calculated by equation (5). The procedure used in obtaining the interfacial contact angles was practically the same as in the last case mentioned, the only difference being the use of organic liquids which form zero contact angles with silica in place of the ones which form finite angles. Thirteen such organic liquids were used. Eight of them had been used in previous investigations but were used in this work so that the results might be compared with those obtained by other methods. The results are given in Table IV.

TABLE III

Adhesion Tension Determinations of Water against Silica By Measurement of Interfacial Contact Angles

(Water—Organic Liquid—Silica)

	P grams/cm ²	θ_{23}	$\cos \theta_{23}$	S_{23} dynes/cm	A_{12} dynes/cm
Acetylene tetrabromide	221	28°29'	0.879	38.32	76.4
Alpha Brom-naphthalene	242	27°15'	0.889	41.57	76.6
Alpha Chor-naphthalene	245	21°52'	0.928	40.24	76.3
Bromoform	261	9°15'	0.987	40.35	77.2
Iodobenzene	260	16° 3'	0.961	41.34	76.9
				Average	76.7

TABLE IV

Adhesion Tension Determinations of Zero Contact Angle Liquids against Silica

Water $A_{13} = 76.7$ dynes/cm. $K = 1.07$

Water—Organic Liquid—Silica

 $r = 3.11 \times 10^{-4}$ cm

	P grams/cm ²	θ_{23}	$\cos \theta_{23}$	S_{23} dynes/cm	S_2 dynes/cm	A_{12} dynes/cm	K^*
Butyl acetate	79.8	22°20'	0.925	13.2	24.1	64.5	2.68
Nitrobenzene	125	41°25'	0.750	25.3	43.3	57.7	1.33
Chloroform	192	22°11'	0.926	31.6	26.5	47.4	1.79
Benzene	215	19°16'	0.944	34.7	28.2	44.1	1.56
Toluene	221	21°57'	0.928	36.5	28.1	43.2	1.54
Carbon disulfide	226	44°16'	0.716	48.1	31.2	42.3	1.34
Ethyl benzene	233	22°20'	0.925	38.4	28.5	41.2	1.45
Chlorobenzene	240	15°36'	0.963	37.9	32.6	40.2	1.23
Propyl benzene	241	23°13'	0.919	40.0	28.6	40.0	1.40
Brombenzene	245	19°20'	0.944	39.6	35.9	39.3	1.09
Butyl benzene	249	24°3'	0.913	41.6	28.8	38.7	1.34
Carbon tetrachloride	265	24°46'	0.908	44.5	26.1	36.3	1.39
Hexane (synthetic)	333	4°35'	0.997	51.0	18.2	25.9	1.42

* $K = A_{12}/S_2$ (or $A_{12} = KS_2$)

Discussion of Results

In Tables V and VI are given adhesion tension values for a series of liquids against silica obtained by the original pressure of displacement method,¹ values obtained by the single transparent capillary tube method,⁷ and values obtained by the present "receding contact angle pressure of displacement" or so-called "pull" method.

Reasonably good agreement is noted throughout for the adhesion tension values of contact angle forming liquids listed in Table V. The adhesion tension values obtained for water against silica show good agreement for the single capillary method and the "pull" method, the average values being 75.8 and 76.7 dynes/cm, respectively. The corresponding value obtained with the original pressure of displacement method was 81.5 or about 6 dynes/cm higher. This difference in values can be attributed to one of two things, either (1) the free surface energy of the silica (tripoli) used in the original investigation was different from that of the fused quartz and the sand of the other investigation, or (2) the higher value for the adhesion tension of water obtained in the original investigation was due to experimental errors in that work. The value obtained was dependent upon results of work with one contact angle forming liquid only, namely, alpha bromnaphthalene. An error in the determination of the interfacial contact angle of alpha bromnaphthalene against water would account for the difference in values obtained. This work

⁷ Bartell and Merrill: J. Phys. Chem., **36**, 1178 (1932).

TABLE V

Comparison of Adhesion Tension Values obtained by Different Methods
Contact Angle Forming Liquids against Silica

	Original Pressure Method A_{12}	Single Capillary Method A_{12}	Present Method A_{12}
Acetylene tetrabromide		43.3	42.8
Alpha Brom-naphthalene	41.1	41.1	39.6
Alpha Chlor-naphthalene		39.8	39.0
Bromoform		37.3	37.4
Iodobenzene		38.2	37.2

Water against Silica

(Water—Organic Liquid—Silica System)

	A_{13}	A_{13}	A_{13}
Acetylene tetrabromide		76.3	76.4
Alpha Brom-naphthalene	81.5	75.9	76.6
Alpha Chlor-naphthalene		76.2	76.3
Bromoform		75.3	77.2
Iodobenzene		75.5	76.9
Average	81.5	75.8+	76.7

has been rechecked and we have no good evidence of any error in the original work. It seems then that the most logical conclusion is that the original silica used (tripoli) possesses surface properties different from those of fused quartz and of sand.

In Table VI are given adhesion tension values obtained by each of the three methods for a series of organic liquids against silica. Again it is noted that good agreement was obtained with the single capillary method and the

TABLE VI

Comparison of Adhesion Tension Values obtained by Different Methods

Zero Contact Angle Liquids against Silica

Water—Organic Liquid—Silica

	Previous Pressure Method	Single Capillary Method	Present Method
Butyl acetate	72.1	66.6	64.5
Nitrobenzene	61.4	57.3	57.7
Chloroform	58.7	45.4	47.4
Benzene	51.2	46.5	44.1
Toluene	53.4	46.5	43.2
Carbon disulfide	43.2	40.5	42.3
Carbon tetrachloride	39.5	35.6	36.3
Hexane (synthetic)		29.9	25.9

"pull" method while the values obtained with the original method are uniformly higher. These higher values are to be expected if one considers that the values obtained for each of these liquids is dependent upon the value for water used in the calculation.

Were the value of 76 to be accepted as the adhesion tension value for water against tripoli (as it appears to be for the other forms of silica), then the adhesion tension values for the other liquids against it would be practically the same as obtained for them against fused quartz and sand. As above stated we have no good reason to believe that the earlier work is seriously in error, so we shall conclude for the present that the surface properties of the different forms of silica are different. This latter view appears to be justified from more recent work in this laboratory which is as yet unpublished in which it has been shown conclusively that the surface properties of surfaces such as of silica are dependent upon the precise treatment to which they are subjected.

Work of Adhesion. Water vs. Solid Surfaces against a Series of Organic Liquids. It was found by Bartell and Hershberger⁸ that decreases in free surface energies which occur when a polar solid and each of a series of liquids are brought together are in the same direction and of the same relative magnitude as the decreases which occur when the same series of liquids are brought into contact with water. Harkins and Dahlstrom⁹ have observed that: "the energy relation at the interface between solid oxides and organic liquids are similar to those between water and the same organic liquids."

The data obtained in the present work tends to substantiate these generalizations and has shown further *a definite relationship between the work of adhesion of a series of organic liquids for silica and for water.* The work of adhesion, W_a , represents the change in energy (ΔF) which occurs when a given phase, as a solid, comes in contact with a liquid, *i.e.*,

$$\Delta F = W_a = S_1 + S_2 - S_{12}. \quad (6)$$

Similarly when an organic liquid surface and a water surface come together the free surface energy relations may be expressed as follows:

$$\Delta F' = W_a' = S_3 + S_2 - S_{23}. \quad (7)$$

The free surface energies of a solid-air or of a solid-liquid interface are not determinable but the decrease in free surface energy which occurs when a solid-air interface is replaced by a solid-liquid interface is represented by the adhesion tension of the liquid against the solid. It is therefore permissible to use the following equation:

$$\Delta F = W_a = A_{12} + S_2. \quad (8)$$

By the substitution of appropriate data in equation (8), the work of adhesion of an organic liquid against silica can be calculated. Such calculations were made for all the organic liquids used in this work and the results are given in Table VII. Similarly from equation (7), the work of adhesion of these same

⁸ Ind. Eng. Chem., **22**, 1304 (1930).

⁹ Ind. Eng. Chem., **22**, 897 (1930).

organic liquids against water was calculated. Also the ratios of the work of adhesion of the organic liquids against silica to the work of adhesion of the same liquids against water were calculated and are given in the last column of Table VII.

TABLE VII

Comparison of the Work of Adhesion of Organic Liquids against Silica and of the Same Liquids against Water

Organic Liquid against Silica $W_a = S_1 - S_{12} + S_2$ or $W_a = A_{12} + S_2$	Organic Liquid against Water $W_a' = S_3 - S_{23} + S_2$. ($S_3 = 72.1$ ergs.)						
	A_{12} ergs	S_2 ergs	W_a ergs/cm ²	S_{23} ergs	$S_3 - S_{23}$ ergs	W_a' ergs/cm ²	W_a/W_a'
Nitrobenzene	57.7	43.3	101.0	25.3	46.8	90.1	1.12
Acetylene tetrabromide	42.8	49.1	91.9	38.3	33.8	82.9	1.11
Butyl acetate	64.5	24.1	88.6	13.2	58.9	83.0	1.07
Alpha Brom-naphthalene	39.6	44.0	83.6	41.6	30.5	74.5	1.12
Alpha Chlor-naphthalene	39.0	41.2	80.2	40.2	31.9	73.1	1.10
Bromoform	37.4	40.9	78.3	40.4	31.7	72.6	1.08
Iodobenzene	37.2	39.1	76.3	41.3	30.8	69.9	1.09
Brombenzene	39.3	35.9	75.2	39.6	32.5	68.4	1.10
Chloroform	47.4	26.5	73.9	31.6	40.5	67.0	1.10
Carbon disulfide	42.3	31.3	73.9	48.1	24.0	55.6	1.33
Chlorbenzene	40.2	32.6	72.8	37.9	34.2	66.8	1.09
Benzene	44.1	28.2	72.3	34.6	37.5	65.7	1.10
Toluene	43.2	28.1	71.3	36.1	36.0	64.1	1.11
Ethyl benzene	41.2	28.5	69.7	38.4	33.7	62.2	1.12
Propyl benzene	40.0	28.6	68.6	40.0	32.1	60.7	1.13
Butyl benzene	38.7	28.8	67.5	41.6	30.5	59.3	1.14
Carbon tetrachloride	36.3	26.1	62.4	44.5	27.6	53.7	1.16
Hexane	25.9	18.2	44.1	51.0	21.1	39.3	1.12

From this table it can be seen that the relative order of decrease in the values of the work of adhesion from liquid to liquid in a series of organic liquids is the same in the case of both silica and water. From the obtained ratio, W_a/W_a' , it is to be noted that the values representing free surface energy changes must be of the same order for silica and water since the ratio obtained is quite close to unity.

Conclusions which can be drawn from this investigation are that the receding contact angle pressure of displacement method is comparatively rapid, the results are duplicable and the adhesion tension values calculated from the data obtained with this method are reliable adhesion tension values for the systems in question.

Summary

1. A pressure of displacement method was developed for the measurement of receding contact angles formed within the pores of a membrane of compressed powder. The time required to reach a final characteristic pressure value was much shorter than with methods previously used.

2. The adhesion tension values for water against silica calculated from data obtained by this method agree closely with values obtained by the single capillary method. They are about 6 dynes/cm lower than the values obtained by the previous pressure of displacement method.

3. The adhesion tension values and the contact angle values obtained by this method for liquids which form contact angles with silica are in close agreement with values obtained by the single capillary method.

4. The adhesion tension values of various organic liquids (including zero contact angle forming liquids) against silica determined in this work agree closely with those obtained with the single capillary method and are consistent with those obtained in previous displacement pressure work.

5. The adhesion tension values against silica of several organic liquids not previously used have been determined.

6. Further evidence has been obtained that the free surface energy changes which occur when given organic liquids come in contact with polar solids are of the same relative order as the corresponding energy changes which occur when these same liquids come in contact with water. The ratio of the work of adhesion of an organic liquid with silica, W_a , to the work of adhesion of the organic liquid with water, W_a' , is a constant whose value is close to unity (ave. value = 1.1+).

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